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ERRATA

"On page 18 in Table 3 read 13·3 and 4·32 instead of 3·3 and 43·2"

STUDY OF THE COMPLEX FORMATION BETWEEN MERCURIC CHLORIDE AND SOLUBLE CHLORIDES BY THE ELECTRICAL CONDUCTIVITY METHOD

Part I. Complex Chloromercuric Acids

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(*Read on 26th April,* 1947)

ABSTRACT

The complex formation between mercuric chloride and hydrochloric acid has been investigated by the electrical conductivity method. It has been concluded that the complex compounds, $HCl, HgCl_2$; $2HCl, HgCl_2$ and $4HCl, HgCl_2$ exist in solution.

The enhanced solubility of mercuric chloride in presence of hydrochloric acid was noted by Rose[1], and later Le Blanc and Noyes[2] inferred the formation of complex ions in solution. - Various workers, notably Ditte[3] and Sherill[4] studied the composition of these complexes. Numerous workers have tried the isolation and analysis of the complex compounds, but the results obtained are still not convincing. In recent years, Krishnamurti[5], Braune and Englebrecht[6], and Bernstein and Martin[7] have adopted physico-chemical methods for the study of the composition of the complexes formed in solution, and their results together with those obtained by Nayar and Saraf[8] lead us to believe that in all cases $HHgCl_3$ is formed in the solution.

1

In this paper, we have studied this problem from electric conductivity measurements.

EXPERIMENTAL

The electrical conductivity for an M/100 mercuric chloride solution diluted with an equal volume of water was 6.343×10^{-6} mhos at 30°.

The electrical conductivity of hydrochloric acid solutions of different concentrations were determined. The results are tabulated below :

TABLE I

Temperature 30°

Concentration of hydrochloric acid solution	Electrical conductivity in 10^{-3} mhos.
M/10	37·88
M/20	19·78
M/30	13·14
M/40	9·793
M/45	8·680
M/50	7·564
M/60	6·384
M/70	5·619
M/80	4·866
M/90	4·362
M/100	3·937
M/110	3·670
M/120	3·289
M/130	2·966
M/140	2·880
M/150	2·646
M/160	2·495
M/180	2·120
M/200	2·064
M/240	1·642
M/280	1·369

TABLE II

Temperature $30°$

Final concentrations of the constituents in the mixture		Ratio HgCl$_2$: HCl			Electrical conductivity in 10^{-3} mhos.
HgCl$_2$	HCl				
M/200	M/10	I	:	20·0	37·904
,,	M/20	I	:	10·0	19·884
,,	M/30	I	:	6·67	13·224
,,	M/40	I	:	5·00	9·989
,,	M/45	I	:	4·44	8·921
,,	M/50	I	:	4·00	8·120
,,	M/60	I	:	3·33	6·600
,,	M/70	I	:	2·86	5·651
,,	M/80	I	:	2·50	4·923
,,	M/90	I	:	2·22	4·606
,,	M/100	I	:	2·00	4·185
,,	M/110	I	:	1·82	3·735
,,	M/120	I	:	1·67	3·355
,,	M/130	I	:	1·54	3·012
,,	M/140	I	:	1·43	2·937
,,	M/150	I	:	1·33	2·703
,,	M/160	I	:	1·25	2·589
,,	M/180	I	:	1·11	2·202
,,	M/200	I	:	1·00	2·173
,,	M/240	I	:	0·83	1·670
,,	M/280	I	:	0·71	1·393

DISCUSSION

The electrical conductivity of the mixture in a complex forming system depends on the number of ions formed by complex formation, and also on the respective ionic mobilities of the new ions. Any deviation from the additive values may be ascribed to be due to the complex formation. With this criterion, we have in the following table calculated the percentage change in electrical conductivities of mixtures of mercuric chloride and hydrogen chloride of various compositions, due to the formation of complex ions.

TABLE III

Composition of the mixture $HgCl_2$: HCl	Sum of the conductivities of the constituents in 10^{-3} mhos.	Observed conductivity of the mixture in 10^{-3} mhos.	Difference in 10^{-4} mhos.	Percentage difference.
1 : 20·0	37·88	37·904	1·04	0·28
1 : 10·0	19·78	19·884	1·04	0·53
1 : 6·67	13·14	13·224	1·84	1·40
1 : 5·00	9·799	9·989	1·90	1·94
1 : 4·24	8·606	8·921	3·15	3·66
1 : 4·00	7·670	8·120	4·50	5·86
1 : 3·33	6·390	6·600	2·10	3·28
1 : 2·86	5·615	5·651	0·36	0·64
1 : 2·50	4·872	4·923	0·51	1·04
1 : 2·22	4·368	4·606	2·38	5·45
1 : 2·00	3·943	4·185	2·42	6·14
1 : 1·82	3·676	3·735	0·59	1·60
1 : 1·67	3·305	3·355	0·50	1·51
1 : 1·54	2·972	3·012	0·40	1·34
1 : 1·42	2·885	2·937	0·51	1·76
1 : 1·33	2·652	2·703	0·61	1·92
1 : 1·25	2·501	2·589	0·88	3·52
1 : 1·11	2·126	2·202	0·76	3·57
1 : 1·00	2·070	2·173	1·03	4·97
1 : 0·83	1·648	1·670	0·22	1·33
1 : 0·71	1·375	1·393	0·18	1·30

From the results given in table IV, we have plotted a graph showing the change of percentage difference with composition of the mixture. It is seen from the graph that the maxima points correspond to the following ratios of $HgCl_2$: HCl – 1 : 1 ; 1 : 2 and 1 : 4. Thus we have evidence of the complex compounds, $HgCl_2$, HCl; $HgCl_2$, $2HCl$ and $HgCl_2$, $4HCl$ in the solution.

We therefore conclude, that the compounds formed by the complex formation between mercuric chloride and hydrogen chloride are different in composition, depending on the concentrations of the constituents.

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FIXATION AND LOSS OF NITROGEN AND THE SOURCE OF SOIL NITROGEN

BY N. R. DHAR

Russell[1] has reported that the nitrogen content of the soil in wheat plot 2 B in Rothamsted in 1865 was 0.196% *i.e.* 4850 lbs. of nitrogen per acre and in 1914 the total nitrogen went up to 0.236% *i.e.* 5590 lbs. total nitrogen per acre when farmyard manure at the rate of 14 tons containing 200 lbs. of nitrogen were added per acre. From our experiments with cowdung we find that the ratio of C : N is 20 or 21 : 1. Assuming 20 : 1 as the C : N ratio of farmyard manure in Rothamsted, the amount of carbon introduced in Rothamsted is approximately 4000 lbs. per acre. Our experimental results with nitrogen fixation using cowdung as the energy material show that when the total nitrogen content of the system is 0.180%, the efficiency i.e. the amount of nitrogen fixed per 1 gm. of carbon oxidized is 14.6 milligrams in the light and 7.7 mg. in the dark. We have also observed in all our experiments on nitrogen fixation that the efficiency falls off as the intitial N content increases. It is expected that in Rothamsted where there is less sunshine that the efficiency in sunlight is likely to be 10 mgm. and 5 mgm. in the dark with a soil containing 0.196% N as in 1865. It appears that out of a total of 4000 lbs. of carbon added in the form of farmyard manure, 3000 lbs. may be oxidized per year and may fix 30 lbs. of nitrogen per acre per year. In subsequent years when the nitrogen content of the soil increases the efficiency will fall off and the nitrogen fixation per year may drop down to 15 to 20 lbs. per year. In 49 years from 1865 to 1914 the average nitrogen fixation or increase per year was actually 15.1 lbs. per acre. The same soil contained 0.2210% nitrogen *i.e.* 5235 lbs. nitrogen per acre in 1893 whilst in 1843, it was 0.122% corresponding to 2890 lbs. per acre. Hence the nitrogen fixed per acre is 2345 lbs. in 62 years i.e. 37.8 lbs. per year. In Woburn using 100 lbs. of nitrogen in the form of farmyard manure to a field containing 0.156% nitrogen upto 1888 the total nitrogen increased to 0.171% in the

years from 1876 to 1888. This experiment, therefore, shows a gain of 13 lbs. of nitrogen per year.

On the other hand, when 43 lbs. of nitrogen as ammonium sulphate were added with minerals the soil nitrogen which was 0.122% i.e. 2890 lbs. per acre in 1843 fell to 0.1107% i.e. 2629 lbs. per acre in 1893. Nitrogen added in the form of manures in 50 years was 2150 lbs. and the crop took up 40 lbs. per year. Rain and seed supplied 350 lbs. in 50 years. Hence there is a dead loss of 760 lbs. in 50 years i.e. 15.5 lbs. per year even when manured with 43 lbs. of nitrogen per year in Rothamsted. On the addition of 86 lbs. of nitrogen per year the soil contained 0.119% i.e. 2818 lbs. per acre. Hence the loss from the soil is 72 lbs. of nitrogen in 50 years during which period 4300 lbs. of nitrogen were added as ammonium sulphate and the crop consumed 44 lbs. per year i.e. 2200 lbs. in 50 years. Rain water and seed also supplied 350 lbs. Hence the dead loss in this case is 50.5 lbs. per year. Moreover on the addition of 129 lbs. of nitrogen as ammonium sulphate per year the soil nitrogen rose to 0.129% i.e. 3055 lbs. per acre in 1893, whilst in 1843 it was 0.122%. Hence in this case the gain in soil nitrogen is only 165 lbs. in 50 years. The manure added 6450 lbs. and rain and seed another 350 lbs. Hence the total added nitrogen is 6965 lbs. out of which the crop took 46 lbs. per acre per year i.e. 2300 lbs. in 50 years. In this case on the addition of 129 lbs. of nitrogen as ammonium sulphate, the dead loss in 50 years is 4318 lbs. i.e. 93 lbs. per acre per year.

On the other hand in the unmanured plot the nitrogen content in 1893 was 0.0990% i.e. 2345 lbs. per acre whilst the original nitrogen was 0.122% i.e. 2890 lbs. per acre. Hence in this case the fall in nitrogen in the soil in 50 years is 545 lbs. The crop was using 17 lbs. per acre. Hence the nitrogen balance is as follows :—

Taken up by the crop.	Rain water and seed.	Difference.
850 lbs.	350 lbs.	500 lbs.

whilst the soil lost 545 lbs. Hence the dead loss is only one pound per year per acre.

It is clear, therefore, that when about 100 lbs. of nitrogen are added in the form of ammonium sulphate even in England more than 60 lbs. is lost without benefit to the crop or the soil and the majority of the nitrogen

added is lost. In India the loss is certainly greater as our experiments with ammonium sulphate reveal.

If intensive cultivation is done and if the soil nitrogen has to be maintained at a steady level we should be prepared to add nitrogen as ammonium sulphate to the extent of 100 lbs. of nitrogen per acre for a good crop yield but about 2/3rd of it may be lost as gaseous nitrogen. This loss is mainly due to the formation and decomposition of the unstable substance ammonium nitrite in the processes of ammonification and nitrification, which are oxidation reactions.

Russell and Voelcker[2] have emphasised that in Woburn experiments there were residual effects even of ammonium sulphate and sodium nitrate, although this has not been observed in Rothamsted. These observations can be readily explained from the viewpoint that when sodium nitrate, ammonium sulphate or any nitrogenous matter is added to the soil the crop will obtain their nitrogen requirements from these manures and not from the soil as happens when crops are grown in unmanured fields. Moreover, as there is more crop in the manured fields, the plant residues left in the fields after harvesting are larger in amount than in unmanured fields and hence more nitrogen fixation is possible in manured fields than in the unmanured ones. In foregoing pages it has been stated that when ammonium sulphate at the rate of 43 lbs. 86 lbs. and 129 lbs. per acre has been added annually the nitrogen content of the soil after harvesting the crop is greater than in the unmanured field and hence the crop produced in subsequent years will be larger in the former ones even without application of manure than in the latter. This is supported by the Rothamsted results showing that the total N content of the unmanured field is 0·095% against 0·099% using artificial manures.

It is well known that the chief object of starting the Woburn experimental station was to test experimentally whether the dung obtained from animals fed on decorticated cotton cake has better manurial value on soils than the dung obtained from corn feeding. After 50 years experiment Russell and Voelcker[3] stated as follows :

" A review of the results forces one to the conclusion that the experiments have entirely failed to show any marked superiority of cake feeding over corn feeding on this soil ".

These unexpected results have not yet been explained by the workers in Rothamsted or Woburn but will be quite clear from the following considerations :

In the Woburn experiments in the cake 45 lbs. of NH_3 *i.e.* 37 lbs. nitrogen were added per acre, whilst with corndung 18 lbs. NH_3 added *i.e.* 14·8 lbs. nitrogen were added.

Now if we take C : N ratio in corndung as 30, then the carbon added is 444 lbs. per acre, out of which approximately 1/4th *i.e.* 111 lbs. remains in the soil. Then about 330 lbs. of carbon is oxidised in the soil per year. This may lead to a fixation of 6 lbs. of nitrogen. Hence the total nitrogen in the corndung is 6 + 15 lbs. = 21 lbs. per acre. Even if we assume that the C : N is 20 : 1 in corndung, the carbon added is 296 lbs. per acre and if 150 lbs. are oxidised yielding 2 lbs. of fixed N and making a total of 17 lbs. of nitrogen per acre. The soil contains nearly 0·156% *i.e.* 3500 lbs. total nitrogen and hence the total nitrogen in the cake dunged field is 3500 + 37 lbs. = 3537 lbs. and in corndunged field is 3500 + 21 lbs. = 3521 lbs. per acre. If we assume that about 2% of the total nitrogen is in the available form, then the available nitrogen becomes 70.7 ibs. per acre in the cake dunged field and 70.4 lbs. in the corndunged field and thus the crop should be identical.

Even when the total nitrogen of the soil drops to 0.093% after continuous cultivation, the total nitrogen in the soil becomes 2082 lbs. per acre and if 2% is in the available form, then the available nitrogen becomes 41.6 lbs. per acre. But if we add the cake dung or corn dung, the total nitrogen in the cake dung becomes 2082 + 37 lbs. = 2119 lbs. making 42.4 lbs. available nitrogen per acre, whilst with corn, the total nitrogen and available nitrogen become 2103 lbs. and 42 lbs. respectively. This also should produce the same crop. On the other hand, if nitrogen is added in the form of ammonium sulphate or sodium nitrate instead of the cake the position becomes different atonce as will be evident from the following lines :—

The original available nitrogen present in the soil is 70 lbs. per acre, whilst the available nitrogen added is 37 lbs. (equivalent to the cake dung) and this makes 107 lbs. per acre, whilst with corn dung equivalent of nitrogen added as ammonium sulphate or sodium nitrate, the total avai-

lable nitrogen comes upto $70 + 15$ lbs. $= 85$ lbs. These amounts of available nitrogen should produce better crops than with dung, more so with the first case than in the second but both the crops should be better than with dungs. This is corroborated by the Woburn experiments.

SOURCE OF SOIL NITROGEN COMPOUNDS

According to Hall[4] leguminous plants or rather the bacteria with which they are associated are probably the original source of world's stock of combined nitrogen. Russell[5] has stated "In England they had established that the source of nitrogen in the soil was leguminous plants. But in the arid regions of U.S.A. they failed to get clear evidence of fixation by leguminous plants". On the other hand Dhar[6] has emphasised that the nitrogen status of a soil is permanently increased by the addition of cow-manure (farmyard manure) or other carbonaceous substances e.g. molasses, leaves, hay etc. which are oxidised in the soil causing nitrogen fixation but not by legumes which do not leave a residual effect on the soil for long. The sources of soil nitrogen is this fixation of atmospheric nitrogen and the added nitrogenous matter present in plant residues.

This conclusion of Dhar is supported by the following classical observations made at Rothamsted and Woburn. The Hoos field (Rothamsted) experiments with red clover were continued from 1849 to 1877 during which clover was sown 15 times but only produced a crop in seven years. This land was divided into a number of small plots from 1878 and sown with various leguminous plants like lucerne, peas, beans, vetches etc. At first a fair growth of some of the plants was obtained on the land which had ceased to carry red clover but in later years there were repeated failures of growth. The land got very foul and in a poor mechanical condition. Hence in 1898 the greater part of the land was sown with wheat without manure and the result showed that the leguminous crop left residual nitrogen in the soil but this residue was rapidly exhausted and after five years there was hardly any effect left. It appears, therefore, that the continuous growing of leguminous crops is a difficult business and the residual effect lasts for a short time. On the other hand, the residual effect of farmyard manure is far more permanent. Thus one of the permanent barley plots in Rothamsted received 14 tons of farmyard

manure containing 200 lbs. of nitrogen per year from 1852 to 1871. It was then divided into two plots one of which received no manure of any kind, and the other continued to receive farmyard manure. The produce in the barley plot on the half receiving no manure since 1872 was double of that obtained from the continuously unmanured plot even after 30 years. In Rothamsted experiments with hay, farmyard manure was applied for the first 8 years at the rate of 14 tons per acre. The application was discontinued but the beneficial effects lasted for 40 years. Similar lasting residual effect of farmyard manure has been reported in the Woburn experiments.[7] Moreover, a plot of land in the Geescroft field (Rothamsted) covered with grass without any leguminous plant showed an increase in nitrogen from 0.108 to 0.145 % in 20 years i.e. 44 lbs. of nitrogen per acre per annum. The following results were obtained on Broadbalk plots to which ammonium sulphate was annually added since 1844 and sodium nitrate since 1852. The original nitrogen in the soil was probably 0.122%.

	Ammonium sulphate				Sodium nitrate		Farmyard manure
Nitrogen added per acre in lbs.	None	43	86	129	43	86	200
Nitrogen in soil % in 1914.	0.104	0.111	0.119	0.129	0.116	0.115	0.236

It appears therefore, that there was deterioration of soils with 43 lbs. and 86 lbs. but with 129 lbs. nitrogen added as ammonium salt or nitrate the nitrogen of the soil remained practically stationary, whilst farmyard manure which can fix atmospheric nitrogen improved the soil status markedly. Leguminous crops with a C/N ratio of about 12 to 13 adds total nitrogen temporarily and this is nitrified fairly quickly and the available nitrogen thus produced is partially absorbed by the crops and partially lost as nitrogen gas. In this respect they resemble artificial farmyard manure (compost.) Because of the presence of carbonaceous compounds in the leguminous crops the nitrification of the nitrogenous compounds is retarded to a certain extent and hence the residual effect may last for 2 to 5 years whilst with ammonium salts there is hardly any residual effect even in the second year. Farmyard manure, however, with a C/N ratio of 20 or more has been found to fix atmospheric nitrogen and the carbonaceous compounds in farmyard manure preserve the soil nitrogen from rapid nitrification and loss by acting as negative

catalysts in the ammonication and nitrification processes, which are oxidation reactions and the residual effect may last for a very much longer period. The leguminous crops are plants of a very special variety and have to be aided by bacillus radicicola or other symbiotic bacteria for nitrogen fixation. These plants and bacteria do not occur in all soils. Hence it is difficult to assume the presence of these plants and bacteria in newly formed soils where nitrogen fixation takes place readily and this process may be a physico-chemical and non-biological reaction aided by light absorption. At a later stage in the evolution of the soil, Azotobacter and bacillus radicicola with legumes may appear and help in the soil enrichment. The recent report of Keen[8] that the residual effect of artificial manures in Cyprus is more pronounced than organic manures is contrary to the experiences in India, Ceylon, South Africa, French Morocco and Greece but his observations on the additions of organic matter to tropical soils are explicable from the viewpoint advanced here.

SUMMARY

(1) Experimental results on manuring show that ammonium sulphate or sodium nitrate only improves crop production but does not increase soil fertility and the total nitrogen content of the soil. When 100 lbs. of nitrogen per acre of arable land are added as ammonium sulphate almost 65 lbs. are lost without benefit to the soil or crop.

(2) Cow dung, farm yard manure, leaves, molasses, hay etc. containing carbonaceous compounds not only fix atmospheric nitrogen and enrich the soil but act as a preserver of the nitrogenous compounds by functioning as negative catalysts in the processes of ammonification and nitrification, which are oxidation reactions. The loss of soil nitrogen is mainly due to the rapid nitrification of nitrogen compounds with the formation and decomposition of the unstable substance ammonium nitrite. Hence organic manures improve crop production and also the fertility of the soil permanently.

(3) It appears that the source of the world's stock of combined nitrogen in the soil is the fixation of atmospheric nitrogen by the oxidation of carbonaceous compounds present in the organic manures and the added nitrogenous compounds present in the plant residues. Farm yard manures leave beneficial effects on soils for 30 or even 40 years after their

addition, whilst legumes can have residual effect for not more than five years.

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(1) Russell-Soil conditions and Plant Growth page 361 (1932).

(2) Russell and Voelcker 50 Years of Field Experiments at Woburn page 51.

(3) Ibid page 23.

(4) A. D. Hall "Book of Rothamsted Experiments", year 1905, p. 14.

(5) Russell Address at Bangalore, Dec. 15, 1936.

(6) Dhar 'Nature' *151*, (1943), 590.

(7) Russell and Voelcker "50 Years of Field Experiments at Woburn" pages 158-161.

(8) B. A. Keen "The Agricultural Development of the Middle East", 1946, pages 48, 117-119.

OXIDATION OF EDIBLE SUBSTANCES BY HYDROGEN PEROXIDE WITH IRON AS CATALYST

By N. R. Dhar and B. V. S. Raghavan

(*Read on 15th September*, 1947)

Edible substances like fats, carbohydrates and proteins are easily oxidized in the animal body. In normal health slow and simultaneous oxidation of food materials containing fats and carbohydrates and proteins takes place but in diabetes glucose, which is the chief energy material under normal conditions does not take part in the oxidation. Hence the oxidation of the other materials like proteins and fats has to be hastened in the human body and this produces acetone bodies harmful to the system.

In this laboratory Chakravarti and Dhar[1] carried on experiments with hydrogen peroxide as oxidising agent in presence of ferric salt as a catalyst and in this paper our observations and results are recorded in extending the same line of investigation with other food materials.

EXPERIMENTAL

(a) 0.5 gr. of the organic substance was mixed with 50 cc. water to which 10 cc. of 11·2 vol. hydrogen peroxide were added with 1cc. of ferric sulphate, containing 0.005 gr. of iron. The mixture was kept at 50° for 60 hours. Then it was distilled and to the distillate which was free from hydrogen peroxide, 10 cc. of N/10 caustic soda and 10 cc. of N/10 iodine were added and was set aside for 10 minutes and the amount of iodine used up was estimated.

(b) 0.5 gr. of oil and 0.5 gram of dextrose were taken and 15 cc. of carbon tetrachloride were added. Then 50 cc. of a mixture containing equal volums of 5% alcoholic iodine and 6% alcoholic mercuric chloride which were mixed a day before were added to the oil and dextrose mixture which was left overnight and the amount of iodine used up per 100 gr. of oil was estimated.

(c) 0.5 gr. of oil was taken and 10 cc. of hydrogen peroxide and 1cc. of the same ferric sulphate solution and 50 cc. of water were added to the oil and this mixture was kept at 50° for 60 hours. Then it was distilled free from hydrogen peroxide and the residue was treated in the manner described in (b). The difference between (b) and (c) gives the amount of oil oxidised in terms of iodine. A small correction has to be applied for the amount of iodine taken up by dextrose in (b) and with 0.5 grm. dextrose 0.02 gram of iodine was absorbed.

It was observed by Dhar and collaborators[2][3] and by Moureu and Dufraisse[4] that the slow oxidation of substances is retarded by reducing agents which usually undergo oxidation along with the primary change.

Not only fats and proteins produce compounds of aldehydic and ketonic nature but the carbohydrates as well. The explanation is not far to seek. The carbohydrates on oxidation give rise to glyceric aldehyde and lactic acid and these produce acetaldehyde[5]. The higher fatty acids gradually undergo oxidation to compounds containing smaller amounts of carbon by β-oxidation[6] and finally to butyric acid which may give rise to acetone bodies. Proteins hydrolyse and give alanine and other amino-acids. These in turn produce acetaldehyde and other aldehydic bodies.

Oxidation of sodium tartrate, sodium citrate, sodium oxalate, sodium acetate, butter, ghee, gingeli oil, castor oil, cocoanut oil, groundnut oil, mustard oil, lactic acid, stearic acid, sodium palmitate, sodium oleate, yellow of the egg, white of the egg, and dextrose was studied and also the effect of varying the amount of dextrose from 0.5, 1, 1·5, to 2 grs. A glance at the table no 1. shows that sodium tartrate tops in the list in the formation of acetone bodies when it is individually oxidised (table no 1, column no 2.) with hydrogen peroxide. Then come palmitate and oleate, dextrose, and ground nut oil. Ground nut oil and dextrose are comparable in their oxidisability. When oxidised alone yellow of the egg, butter, ghee give small amounts of acetone bodies (0.02gr) stearic acid gives the least amount of acetone bodies (0.005gr.) Yellow of the egg. gives greater amount of acetone bodies than the white (0.0199 against 0.0141gr.)

TABLE I

Amounts of acetone bodies got (in terms of iodine) with o·5 gr substance + carbohydrate.

1 Substance.	2 Acetone bodies with H_2O_2 only	3 Acetone bodies with H_2O_2 + o.5gr Dextrose	4 Acetone bodies with H_2O_2 + 1gr Dextrose.	5 Acetone bodies with H_2O_2 + 1.5 grs Dextrose,	6 Acetone bodies with H_2O_2 + 2grs Dextrose.
Sodium tartrate.	0.1709	0.0034	0.0072	0.0093	0.0098
Sodium palmitate.	0.1370	0.0039	0.0059	0.0079	0.008
Sodium oleate.	0.1094	0.0052	0.0073	0.0092	0.0097
Sodium oleate.	0.0976	0.0046	0.0092	0.0111	0.0113
Sodium acetate.	0.0976	0.0046	0.0092	0.0111	0.0113
Sodium citrate.	0.0939	0.0081	0.0123	0.0141	0.0144
Sodium oxalate.	0.0893	0.0116	0.0152	0.0171	0.0171
Dextrose.	0.0765	....	....	....	....
Ground nut oil.	0.0720	0.0214	0.0234	0.0251	0.0269
Cocoa nut oil.	0.024	0.0059	0.0069	0.0079	0.0079
Lactic acid.	0.0204	0.0069	0.0069	0.0079	0.0079
Mustard oil.	0.0204	0.0073	0.0073	0.0082	0.0079
Castor oil.	0.0204	0.0039	0.0047	0.006	0.0074
Yellow of the Egg.	0.0199	0.0041	0.0047	0.006	0.0074
Butter.	0.0157	0.0059	0.0067	0.0067	0.0079
Ghee.	0.0153	0.0067	0.0059	0.0052	0.0079
White of the Egg.	0.0141	0.0061	0.0063	0.0071	0.0074
Gingeli oil.	0.0139	0.0067	0.0067	0.0073	0.0079
Stearicacid.	0.0059	0.0067	0.0052	0.0073	0.0079

Then 0.5gr. of each of the above substances was mixed with 0.5gr. of dextrose (table no 1, column 3). Sodium tartrate which gives the maximum amount of acetone bodies in the 2nd column now produces minimum amount (0.0034gr against 0.1709gr). In this series of experiments ground nut oil gives the maximum amount of acetone bodies (0.0214gr.) Ghee, butter, mustard oil give acetone bodies of the order of about (0.008gr). Hence the marked effect of dextrose in lowering the formation of acetone bodies.

For example taking the minimum case in column 3, table no 1 *viz*. 0.5gr. of dextrose and 0.5gr. of tartrate give 0.0034gr. of acetone bodies while they ought to give 0.0765 + 0.1709 = 0.2474gr had there been no retardation.

The effect of increasing the amount of dextrose from 0.5, 1, 1·5, to 2 grs. was also investigated (table 1 columns 3,4,5,6). The amount of acetone products formed rises with the increase in the amounts of dextrose (upto 1.5gr. of dextrose) in the case of sodium tartrate, palmitate, citrate

namely with substances which give high amounts of acetone bodies when they are individually oxidised with hydrogen peroxide. With slowly oxidisable substances like butter, ghee changing the amounts of dextrose has relatively smaller effect.

The mixed oxidation of fat, carbohydrate and protein was also studied (table 2). In this series of experiments dextrose and fat together were mixed with the white of the egg or yellow of the egg and the effect was studied. With white the maximum amount of acetone bodies is given by sodium tartrate (0.0134gr column 2 table 2) and the minimum with lactic acid (0.0068gr.) Ghee and butter give about 0.008gr. With the yellow of the egg the maximum is given by tartrate 0.0041gr and the minimum by butter, ghee, and mustard oil (column 3 table 2). Here also the decrease of the acetone body formation in the mixed oxidation of fats and proteins and carbohydrates is apparent. From the table we can see that the amount of acetone bodies got by the yellow of the egg is much smaller than the acetone bodies given by the white (the ratio is about 1 : 3).

TABLE 2

Amounts of acetone bodies got in terms of iodine in the mixed oxidation of 0·5 gr. Fat. + 0·5 gr. protein + 0·5 gr. Dextrose.

Substance	Acetone bodies with 0·5gr. Dextrose + 0·5 white of egg.	Acetone bodies with 0·5gr. Dextrose + 0·5gr. of yellow of egg.
Sodium tartrate.	0·0134	0·0041
Sodium palmitate.	0·0131	0·0039
Sodium oleate.	0·0130	0·0041
Sodium acetate.	0·0125	0·0041
Sodium citrate.	0·009	0·0034
Sodium oxalate.	0·0099	0·0041
Ground nut oil.	0·010	0·0039
Lactic acid.	0·0068	0·0024
Mustard oil.	0·0073	0·0023
Castor oil.	0·0093	0·0023
Butter.	0·0079	0·0023
Ghee.	0·0079	0·0027
Gingeli oil.	0·0093	0·0059
Stearic acid.	0·0084	0·0039
Cocoanut oil.	0·008	0·0031

F. 3

By the iodine value determinations it was studied whether when a fat is mixed with a carbohydrate it is undergoing retardation or not (table 3). From the table of iodine values the difference in the values in the columns 2 and 3 gives the amount of oil oxidised and the difference of the values in columns 5 and 3 gives the amount of retardation.

TABLE 3

Iodine values etc. in the Oxidation experiments performed.

1	2	3	4	5	6
	Iodine used up per 100 grs of oil after correction for dextrose.	Iodine used per 100 grs. of oil with H_2O_2 only.	Amount of oil oxidyzed in terms of iodine.	Iodine used up per 100 grs. of oil + H_2O_2 + Dextrose.	Amount retarded in terms of iodine (after correction for dextrose).
Castor oil.	85·1	69·1	16	73·2	4·12
Cocoanut oil.	9·1	1·21	7·89	2·45	1·26
Ground nut oil.	73·9	18·4	55·5	53·85	25·47
Mustard oil.	100·4	83·2	17·2	88·2	5·02
Butter.	30·1	17·8	12·3	21·2	3·42
Ghee.	29·5	17·4	12·1	20·7	3·32
Gingeli oil.	109·6	96·3	3·3	100·6	43·2

CONCLUSIONS

1. Ground nut oil appears to form as much of acetone bodies as dextrose.

2. The amount of acetone bodies obtained in the mixed oxidation of either fat and carbohydrate or fat, carbohydrate and protein is much smaller than the sum of the amounts of acetone bodies which each gives rise to individually.

3. With substances which form large amounts of acetone bodies when individually oxidised the amount acetone bodies formed tend to rise with increasing amounts of dextrose. With slowly oxidisable substances like ghee, butter etc. rise in the amount of dextrose has not much effect.

4. Yellow of the egg generates 1/3 the amount of acetone bodies which the white gives in the presence of carbohydrate and fat.

These results are in general agreement with those obtained previously in this laboratory.

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INVESTIGATIONS ON NICKEL AMMINES

Part I. *Isolation of Nickel Ammine Thiocyanates*

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ABSTRACT

Two new methods of preparation of Tetra and Tri ammoniate nickel thiocyanate have been described.

INTRODUCTION

It is well known that a solution of ammonium hydroxide when added to cobalt, nickel and copper salt solutions gives a precipitate of the hydroxides of these metals which dissolve in an excess of the reagent forming complex ammines.

A large number of cobalt[1] and copper[2] ammines have been investigated by numerous workers. Some complex ammines of nickel salts notably those of nickel halides, nitrates, sulphate and phosphate, have also been isolated.[3]

The present investigation has been undertaken in order to find out if there exists any co-relation between the composition and properties of the various nickel ammines with those of cobalt and copper.

Nickel thiocyanate tetra ammoniate Ni $(CNS)_2$ $4NH_3$ was first mentioned by Meizendroff.[5] Bohart[6] however found that Meizendroff's compound corresponded to nickel thiocyanate tri-ammoniate. He further prepared nickel thiocyanate ammoniates with 2, 3, 4, $5\frac{1}{2}$ and 8 mols. of ammonia. A tri-ammoniate has also been mentioned by Peters.[7]

The method of preparation of the tetra ammoniate compound used previously was by adding an equivalent amount of ammonium thiocyanate solution to a hot saturated solution of nickel sulphate, then adding ammonia solution till there is a strong smell of ammonia. This solution when left for crystallisation, yielded the tetra ammoniate compound.

In this paper two new methods of isolation of the tetra and the tri ammoniate nickel thiocyanate have been described.

EXPERIMENTAL

The sulphate ion, from nickel sulphate was first removed from a mixture of a nickel sulphate solution containing ammonium thiocyanate, by adding requisite amounts of barium hydroxide solution and simultaneously adding excess of ammonium hydroxide solution. The insoluble barium sulphate was then filtered out and the filtrate set apart for crystallisation.

It was found that the ammonia escaped very quickly and unless the solution was very concentrated it had a tendency to hydrolyse. In the next attempt therefore, nickel thiocyanate was prepared and simultaneously converted to the ammine complex by treating a mixture of solid nickel sulphate and barium thiocyanate with concentrated ammonia solution. The method of obtaining nickel thiocyanate depended on the formation of this compound by the interaction of barium thiocyanate and nickel sulphate in the reaction mixture when barium sulphate separated out. The nickel thiocyanate then reacts with ammonia to give the ammine complex.

To a weighed quantity of nickel sulphate ($NiSO_4 7H_2O$) an equivalent amount of barium thiocyanate was added in the solid state. To this, a measured volume of concentrated aqueous ammonia solution was added, the precipitated barium sulphate filtered off and the filtrate was set apart for crystallzation at a room temperature (30°). After leaving it over night crystals were found to have been formed. These crystals were separated, dried quickly by pressing between layers of filter-paper and in order to avoid loss of ammonia from the crystals, they were kept in a well corked glass tube in a dessicator filled with ammonia vapours, over lime.

It was found that a good yield of the crystals could be obtained by using at least 1/10 th. molar quantity of nickel sulphate, an equivalent amount of barium thiocyanate and atleast 50-60ccs of approximately .11 M ammonia solution. With a more dilute solution of ammonia the filtrate, hydrolyses on standing.

Nickel in the crystals was estimated as the dimethylglyoxime compound, ammonia by the Kjeldhals' method and thiocyanate by the Volhard method.

The analytical results found :

	Nickel	Thiocyanate	Ammonia	Total	Ratio Ni : NH$_3$	Molecular formula.
I.	24.20	47.67	27.68	99.55	1 : 3.971	The ratio of Ni : CNS was found to be 1:2. Water of crystallization absent. Hence Molecular formula Calculated Ni (CNS)$_2$. 4NH$_3$
Calculated.	24.29%	47.72%	27.99%	100.00%	..	

The tetra-ammoniate compound thus obtained by us, smells very slightly of ammonia. Has a saphire blue colour with violet tinge. The surface layer of the salt gradually tarnishes when exposed to air because of the loss of ammonia. The salt is soluble in ammonia solution giving a greenish blue, blue and violet blue solution, depending on the increasing concentration of ammonia.

It will be seen that in the method described above the ammonia compound that crystallizes out is mainly the tetra ammoniate nickel thiocyanate, provided precautions are taken to avoid the loss of ammonia from the crystals. The second crop of crystals from the above which we expected to be a lower ammonia containing compound, when analysed proved to be a mixture of tetra and lower ammonia containing compounds for obvious reasons. Any attempt to prepare pure lower ammonia containing nickel thiocyanate ammoniates, by the same method, by using more dilute solution of ammonia proved fruitless, because of the hydrolysis that occured during crystallization. Hence another method was adopted for the preparation of these complexes by taking nickel carbonate and ammonium thiocyanate as the starting material.

For this, a sample of Merck's nickel carbonate (basic) was taken and its nickel content estimated. To a weighed quantity of nickel carbonate 1/10th. molar, 50ccs of fairly concentrated solution of ammonium thiocyanate (approximately 60% solution) were added, the solution warmed when there was a vigorous effervesence with the evolution of carbon dioxide and some ammonia. The solution was filtered and set aside for crystallization at a room temperature (26°) when small blue crystals separated out

after some time. The crystals were dried by pressing between layers of filterpaper and kept in a well corked glass tube.

The analytical results found are.

Nickel.	Total Analysis. Thiocyanate.	Ammonia.	Total.	Ratio. Ni : NH₃	Molecular Formula
26.2	50.89	21.89	98.98	1 : 2·900	The ratio of Ni: CNS was found to be 1 : 2. Water of crystayllization absent. Hence molecular formula $Ni(CNS)_2.3NH_3$
Calculated.	26.11%	51.32%	22.57%	100.00	..

The triammoniate compound thus obtained by us does not smell of ammonia. Has a blue colour and does not tarnish for some time when exposed to air. The salt is soluble in moderately concentrated ammonia solution giving a greenish blue solution, but hydrolyses like the tetra ammoniate compound in aqueous solution with the precipitation of nickel hydroxide.

CONCLUSION

More work is in progress to isolate pure sample of higher ammine compounds of nickel for a complete study of the various nickel ammine complexes.

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STUDIES IN THE PRODUCTION OF YEAST

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Pasteur in his classical researches on 'Fermentation' described this phenomenon as 'Life without air (La vie sans l'air)' because the chemical change involved in fermentation is as follows :— $C_6H_{12}O_6 = 2\ CO_2 + 2\ C_2H_5OH + 25K$ Cals and free oxygen does not take part directly in the process.

In ordinary fermentation of sugars into alcohol Pasteur was the first to demonstrate that yeast can live in the presence of only small traces of oxygen. Since the growth of yeast is abundant in the process of fermentation and the small amount of oxygen present is used up rapidly, it can be assumed that the greater part of the development of yeast can take place in the absence of free oxygen. The energy requirement of the yeast is met with by the heat of the reaction as stated above.

We have carried on numerous experiments on the production of yeast by using different energy materials and have found that yeast can grow vigorously using even alcohol and starch as energy materials specially when air is passed.

In our experiments on the growth or yeast (Torula variety containing 6.8% N and 22.8% C.) we have used analytically pure starch of 1% strength and have passed a current of air. The temperature was maintained at 30°; without passing air hardly any growth of yeast is observed.

Similarly we have obtained a vigorous growth of yeast by passing air in dilute solutions of alcohol. In this reaction the presence of any carbohydrate is not essential. The dilute alcohol without any other energy material is slowly oxidized by air in presence of yeast and supplies energy according to the following equation :—

$C_2H_5OH + 3O_2 = 2\ CO_2 + 3\ H_2O + 325$, K. Cals. and a part of the alcohol seems to be assimilated by yeast for building its body materials. We believe that the same thing happens with starch. By passing air,

we have been able to grow yeast even in solutions or suspensions of glycerol, gelatine, oils, urea, ammonium sulphate, microcosmic salt, sodium nitrite, sulphur, sulphite, thiosulphate, ferrous oxide, metallic aluminium, zinc, space cobalt, iron etc. used as food materials.

India being chiefly as yet an agricultural country has an abundant supply of raw materials for yeast manufacture $e.g.$, rice, barley, maize, wheat and potatoes, molasses etc.. Another raw material on which so far no attention has been paid is toddy. With the coming of prohibition in the country, toddy may become a useless product. Fresh samples of toddy have been analysed in these laboratories and were found to contain approximately 13.4 gms. of sugar per 100 cc. of fresh toddy which yielded 1.25 gms. of yeast without passing air.

The effect of nitrates and phosphates of sodium potassium and ammonium on the growth of the Torula variety of yeast have been studied. It has been observed that ammonium nitrate increases the yeast growth, sodium phosphate has also a beneficial effect while potassium ions have a slight toxic effect on the growth of yeast. The effect of negative ions like acetates, chlorides, sulphates etc., on the growth of yeast and alcohol formation have also been investigated. It is found that the presence of an excess of sulphate ions in the culture decreases both alcohol and yeast formation. Acetate ions favours yeast formation but retards alcohol production, while chloride ion favours alcohol formation but retards yeast generation. In the control experiments the yield of yeast was 10.2% of the sugar fermented and it increased to 12.05% if acetate ions were present and decreased to 9.75% if sulphate ions were present. Small sugar concentrations were found favourable for yeast growth while at higher concentration there is a tendency for alcohol production in larger quantity.

The effect of toxic substances on the growth of yeast and alcohol production has been studied :—

As, O_3, $CuSO_4$, $Sb_2(SO_4)_3$, $FeSO_4$ and $MgSO_4$ retard the growth of yeast but $ZnSO_4$ in low concentrations accelerates the yeast growth while in higher concentrations retard it.

The effect of light on the growth of yeast has also been studied and it is found that diffused light is beneficial for the growth of yeast.

F. 4.

Very interesting results have been obtained by growing yeast by passing air in medium containing small amounts of alcohol or starch and necessary inorganic salts in the complete absence of sugar:—

Medium	Grs. yeast produced	Tempt. 25 30° Yield of yeast on the wt. of alcohol or starch
750 c.c. of culture medium containing 7.5 gms. alcohol	2.7188	36.25%
750 c.c. of culture medium containing 7.5 gms. of starch	2.1563	28.75%

It is obvious that the energy liberated by the oxidation of alcohol and starch which are exothermal reactions, is utilized by the yeast for its functions of life and growth. This has a great industrial bearing for yeast can be grown in waste liquors from different industries containing small percentages of alcohol which can not be recovered easily by the ordinary methods. We have been successful in decreasing the alcohol content of wines and converting a part of the alcohol into yeast which is an excellent food material. We are in touch with wine-makers and advising them to prepare healthy wines by aerating them and in this process a part of the alcohol is converted into a nourishing food. The Germans live a good deal on beer especially in summer months. German beer is rich in yeast but poor in alcohol.

Experiments are in progress to obtain yeast in large quantities and study the mechanism of alcoholic fermentation and yeast production and to preserve its vitamin contents.

QUANTITATIVE STUDY OF THE EXTENT OF INHIBITION OF THE PRECIPITATION OF STANNIC SULPHIDE IN PRESENCE OF SOLUBLE TARTRATES

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(Communicated by Dr. S. Ghosh, D.Sc., F.N.A.Sc.)

(Read on 26th April, 1947)

Abstract

This paper is a continuation of the work of Dey and Bhattacharya,[1,2,3] on the study of the inhibition of the precipitation of stannic sulphide in presence of various organic acids and their salts. The extent of inhibition in the presence of sodium tartrate has been quantitatively studied. The inhibition has been ascribed. to be due to complex formation.

Introduction

In a recent publication[1] Dey and Bhattacharya have shown complex formation to be the cause of the non-precipitation of stannic sulphide in presence of oxalic acid and oxalates. In other publications[2,3] they have reported, that the same inhibition is possible in presence of other dicarboxylic acids as well. It is well known (cf Rössing[4]) that the addition of oxalic and tartaric acids can be used to keep tin in solution, when antimony can be precipitated as sulphide by sulphuretted hydrogen.

Stannic tartrate was known to exist,[5] since long, and complex formation between tin and tartaric acid was recorded by various earlier workers.[6,7]. Also, the study of complex tartrates has been the subject of many investigations and in recent years Darmois and coworkers,[8] Vaishya and Raman[9] and Biswas[10] have dealt with this topic in considerable detail. In a very recent publication,[11] Bobtelsky and Jordan have

described the results of their investigations on the complex tartrates and citrates of various metals.

During the preliminary experiments, I have observed that tartaric acid itself is unable to act as an inhibitor in the precipitation of stannic sulphide, whereas soluble tartrates show appreciable activity in this respect. In this paper, the results obtained on using sodium tartrate as an inhibitor is described.

EXPERIMENTAL

A solution of Schuchardt's stannic chloride was prepared in normal hydrochloric acid, and tin was estimated gravimetrically. Standard solutions of sodium tartrate of various concentrations were also prepared. A solution M/5 sodium sulphide was prepared by iodometric standardisation. It was noted that M/5 was the minimum strength of sodium sulphide, which could precipitate stannic sulphide completely from the stannic chloride solution. Since the stannic chloride solution was acidic, the mixture after the addition of an equal volume of sodium sulphide remained acidic.

Several test tubes were taken, and in each were delivered 10 c. c. of 0·09389 M of stannic chloride solution. Now 10 c. c. of the tartrate solutions of known concentration were added, and then 10 c. c. of the sodium sulphide solution. The first was filtered immediately after the addition of sodium sulphide, the second after half an hour, the third after four hours, the fourth after eight hours and the fifth after ninety-six hours. Different sets were taken, using different concentrations of the tartrate solution. A blank experiment, using water instead of the tartrate was also performed. The experiments were performed at a room temperature of 30 °C.

The precipitated stannic sulphide was filtered and estimated as oxide. The filtrates were boiled, and a further quantity of 1 c. c. sodium sulphide solution added, this was left overnight and the stannic sulphide now precipitated was filtered and estimated. The sum of the amounts of stannic oxide estimated in the precipitate and the filtrate corresponded to the total amount of tin available in the solution.

In the following table, the results obtained on the inhibition of the precipitation in presence of different quantities of tartrate are recorded.

PERCENTAGE OF INHIBITION

IV Sn : $C_4H_2O_6''$	Time after which filtration was done				
	0 hour	½ hour	4 hours	8 hours	96 hours
1 : 0	2·35%	2·35%	1·90%	...	...
1 : 0·665	11·78	11·50	11·28	10·42	9·28
1 : 1·33	15·24	13·34	12·08	11·29	10·36
1 : 2·66	18·50	15·32	14·12	13·75	12·03
1 : 5·32	33·71	26·21	25·28	23·62	22·51
1 : 10·64	43·31	33·59	30·65	28·01	26·28
1 : 15·96	56·01	42·21	38.73	32·58	29·36
1 : 21·28	69·28	48·73	40·38	36·71	33·05

In all the cases the inhibition is more marked at first, but soon the precipitation commences. After a period of ninety-six hours a considerable portion of the tin is precipitated as stannic sulphide. Here too, as in the case of oxalic acid and potassium oxalate (loc cit) the precipitate varies in nature, and shows a wide range of colours, beginning from yellow to deep brown, depending on the concentration of the tartrate used. When the ratio tin : tartrate is 1 : 10·64, the precipitate becomes highly gelatinous in nature, and resembles a freshly obtained precipitate of ferric hydroxide, in appearance. When the quantity of tartrate was increased further, the system assumed a colloidal character and a considerable portion passed through the filter paper.

In another set of experiments, the stability of the complex was studied, by allowing stannic chloride and tartrate solutions to remain in contact for different lengths of time, and then stannic sulphide was precipitated with sodium sulphide. The precipitate obtained was filtered immediately after the addition of sodium sulphide, stannic oxide was estimated in the precipitate and the filtrate as before. From these experiments it was inferred, that the inhibition does not depend on the period for which the solutions of stannic chloride and sodium tartrate are

allowed to stand together. Thus the complex formed is quite stable and shows no tendency of decomposition, even when allowed to stand for ninety six hours.

SUMMARY

1. The extent of inhibition of the precipitation of stannic sulphide from acidic solutions of stannic chloride have been studied quantitatively.

2. The inhibition has been ascribed to be due to complex formation between stannic tin and soluble tartrates.

3. It has been found that an appreciable quantity of sodium tartrate has to be added to perceive appreciable inhibition of the precipitation.

4. It has been observed that the formation of a colloid precedes complex formation, and the colloidal matter settles with time. The quantity of tin remaining in solution after the coagulation of the colloid gives an idea of the amount of complex formed.

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STUDIES IN THE DYES DERIVED FROM QUINOLINIC ACID AND CINCHOMERONIC ACID AS ADSORPTION INDICATORS IN ARGENTOMETRIC TITRATIONS :

PART II*

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In a recent communication[1], the use of resorcinol quinolein and cinchomeronein as adsorption indicators in the titrations of halide solutions singly has been described. In the present communication the behaviour of these dyes in mixed halide solutions and also, a comparision between the behaviour of these dyes and that of resorcinol phthalein has been studied. Further, the tetrabromo derivatives of these dyes have been prepared and their applicability as adsorption indicators has been investigated.

Titrations of mixed halide solutions.—Belladen and Piazza[2] have observed that although Brilliant Archill C. and Chromotrope F4B are suitable indicators for all the chloride, bromide and iodide ions separately, yet when a mixture of iodide and chloride ions is titrated against silver ions, the end point (pink——>grey green) occurs, when silver nitrate equivalent to only the iodide ions present has been added. The dyes under investigation (resorcionol quinolein and cinchomeronein) are also quite suitable for all.the three halide ions ; but they mark the end point when the total of all the halide ions present in the solution has been precipitated. The addition of ammonium carbonate does not allow the iodide ions to be titrated alone in the presence of chloride ions.

Comparison of the Applicability of these two dyes with fluorescein.—The resorcinol quinolein and cinchomeronein dyes can be employed in ammoniacal as well as acidic solutions. Unlike fluorescein these dyes can

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be employed in the pH range 2 to 12. It has been found that in the case
of ammoniacal solutions, the cinchomeronein indicates the end point
only upto a concentration of N/30 to N/20 ammonia in the solution to
be titrated; whereas in the case of quinolein, the end points are quite
sharp in solutions in which the concentration of ammonia is as high as
N/3 to N/2. Thus the cinchomeronein shows a behaviour midway
between the pathalein and the quinolein and so it can be inferred that the
substitution of the 'CH' group of benezene by the basic 'N' in pyridine
is the controlling factor in the variation of these properties and the near-
ness of the 'N' atom to the carboxylic groups in the quinolein confers
greater contrast to its properties than it does in the case of the cincho-
meronein :
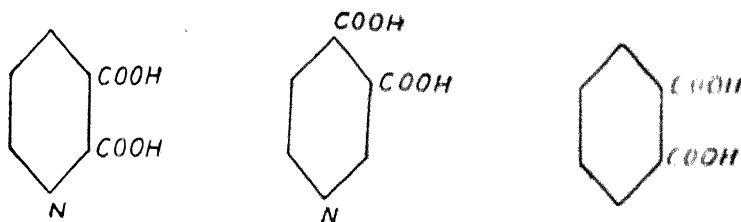
The tertiary 'N' atom, as is well known, has got a powerful
tendency to donate its lone pair of electrons, and this tendency will result
in the formation of a chelate ringed compound, similar to that shown by
Cox and coworkers[3] in the simpler case of argentic picolinate. The
chelation always lowers the solubility of a compound and thus the appli-
cability of these dyes in acidic as well as ammoniacal media can be ex-
plained on the view point of the formation of highly insoluble chelate
compounds with silver.

TETRABROMO RESORCINOL QUINOLEIN AND CINCHOMERONEIN
AS ADSORPTION INDICATORS.

Preparation of the dyes.—The bromination of the quinolein and
cinchomeronein was carried out in the alcoholic solution, and the tetra-
bromo derivatives were prepared and purified. 0·2% solutions of the dyes
were prepared in alcohol and these solutions used as indicators through-
out these investigations.

Titration of Iodide Ions against Silver Ions : When a neutral solution
of potassium iodide is titrated against silver nitrate, the coagulation of

the precipitate begins much before the end point and the precipitate appears as a deep pink mass at the equivalent point. In the case of cinchomeronein, the colour of the coagulated particles remains yellow so long as iodide ions are present in excess and changes to pink with half a drop of the silver nitrate solution in excess, and simultaneously the pink colour of the suspension is discharged. In the case of the tetrabromoquinolein, the particles have a pinkish shade much before the equivalent point, and the end point is indicated merely by the disappearance of the pink colour of the suspension at the equivalent point. However, in acidic or ammoniacal media, the colour change at the end point becomes much sharper with both the indicators. In the acidic solutions, the coagulation occurs just at the equivalent point. So long as the iodide ions are present in excess, the suspension remains yellow and changes sharply to pink at the end point. In the presence of ammonia, the coagulation of the silver iodide begins early. However, the colour on the particles remains yellow with both the indicators and changes to pink with half a drop of the silver nitrate solution at the end point. Along with the colour change on the particles, the pink colour of the supernatant suspension is also discharged simultaneously at the end point.

Titration of Bromide Ions against Silver Ions: When the bromide solutions are titrated against silver ions using tetrabromo-quinolein or cinchomeronein as indicators, no sharp colour change at the end point could be obtained in the neutral solutions. The end points did not improve also by the addition of ammonia. However, in the presence of acetic acid the end points are very sharp and the titrations can be carried out accurately. In the case of the cinchomeronein, the suspension remains yellow and becomes pink just at the equivalent point; whereas in the case of the quionolein, the suspension assumes a slight pinkish shade before the end point and the equivalent point is indicated by change of the colour of the suspension from light pink to deep pink. The end points are made much more sensitive, because the coagulation of the precipitate occurs immediately at the end point.

Titration of Thiocyanate Ions: In the case of the thiocyanate ions also, no sharp end points could be obtained in the neutral as well as in

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ammoniacal media. In the presence of acetic acid, the end points are quite sharp. The coagulation occurs much earlier and the particles assume a slight pinkish shade from the beginning, but there is a sharp colour change from light pink to deep pink on coagulated particles at the end point.

Titration of Chloride Ions : In the case of the chloride ions no sharp colour change could be obtained either in the neutral or in ammoniacal or acidic media. Even in the acidic solutions, the coagulation of the precipitate and the adsorption of the dye occurs much before the equivalent point which indicates that the dye anions are so strongly adsorbed by the precipitated silver chloride particles that they displace even the adsorbed chloride ions.

Titration of Iodide Ions in Presence of other Halide Ions : It is in this field that the indicators have been found to be of practical value. When a mixture of iodide and chloride ions is titrated against silver ions in neutral or acidic media, the end point, indicated by the complete transference of the pink colour of the suspension to the particles of the coagulated precipitate, occurs after the whole of the iodide ions and the chloride ions has been precipitated. However, in the presence of ammonia, the iodide ions alone can be titrated in the presence of chloride ions. When a mixture of the iodide and chloride ions is titrated against silver ions in ammoniacal medium, the coagulation of the silver iodide particles begins soon, but the particles remain yellow. When all the iodide ions have been removed as silver iodide, half a drop of the silver nitrate solution changes the yellow colour on the particles to pink with a simultaneous disappearance of the pink colour of the suspension. The estimation of the iodide ions is accurate, when the ratio of the chloride : iodide ions present has a value upto 1 : 2. In the presence of a greater proportion of the chloride ions, an excess of the silver nitrate solution is required.

Attempts have been made to estimate the iodide ions in the presence of the bromide ions and also of ths bromide ions in the presence of the chloride ions ; but the results were unsatisfactory. Similarly the iodide ions could not be liberated in the presence of the thiocyanate ions.

Volume & conc. of halide solutions	Drops of indicator	Volume & conc. of AgNO$_3$ solution	Transition of colour	Remarks.
10 c. c. of N/10 KI.	2	9·97 c. c. to 9·98 c. c. of N/10 AgNO$_3$.	Pink suspension →Pink precipitate.	Coagulation of the ppt. occurs much before the end point. In case of quin., the particles assume pinkish shade before the end point.
10 c. c. of N/10 KI+4 to 10 c. c. of N HAc.	2	10 to 10·02 c. c. of N/10 AgNO$_3$.	Yellow suspension ⟶ Pink ppt.	The end point is much sharper than in the neutral soln. The coagulation occurs just at the end point.
10 c. c. of N/10 KI+6 to 8 c. c. of N NH$_4$OH.	2	10·0 c.c. of N/10 AgNO$_3$.	Yellow ppt. ⟶ Pink ppt.	The end point is very sharp. Coagulation occurs much earlier, but the end point though occurring on the coagulated particles is quite reversible.
10 c, c. of N/10 KI+5 c. c. of N/10 KCl	2	14.94 to 14·98 c. c. of N/10 AgNO$_3$.	Pinkish suspension ⟶ Pink ppt.	The colour change at the end point is not very sharp. The end point is indicated by the transference of the pink colour from suspension to ppt.
10 c. c. of N/10 KI+3 to 5 c. c. N/10 KCl+ 4 c. c. of. N NH$_4$OH	2	10·0 to 10·04 c. c. of N/10 AgNO$_3$.	Yellow ppt. →Pink ppt.	The end point, though occurring on the coagulated particles, is very sharp. With larger proportions of chloride ions, an appreciable over-consumption of silver ions is required.
10 c. c. of N/10 KCNS +6 to 8 c. c. of N HAc.	2	10·0 c. c. of N/10 AgNO$_3$.	Light pink ppt. →Deep pink ppt.	The end point is very sharp and quite reversible.

SUMMARY

1. A comparision of the applicability of resorcinol quinolein, cinchomeronein, and phthalein as adsorption indicators has been made and the differences have been explained.

2. The behaviour of the indicators in the mixed halide solutions has been investigated.

3. Two new indicators tetrabromo-quinolein and tetrabromo-cinchomeronein have been described.

4. The new indicators are suitable for the titration of iodide, bromide and thiocyanate ions in acidic solutions.

5. The iodide ions can be estimated very accurately in ammonical solutions also.

6. Mixtures of iodide and chloride ions can be analysed completely by the help of these indicators. The whole of the iodide and chloride ions can be determined by titration in neutral or acidic medium, and the iodide ions can be estimated alone by titration in presence of ammonia.

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